ADVANCED COMPUTER SIMULATIONS OF MILITARY INCINERATORS

M.K. Denison*, C.J. Montgomery, A.F. Sarofim, B. Sadler, and M.J. Bockelie
Reaction Engineering International
Salt Lake City, UT 84101

D. Magee	F. Gouldin	J. Bozzelli
Carmagen Engineering, Inc	Cornell University	New Jersey Institute of Technology
Rockaway, NJ 07866	Ithaca, NY 14853	Newark, NJ 07102

ABSTRACT

Incineration is one of the technologies being used by the US Army to destroy the highly toxic chemical agents and munitions contained within the Chemical Weapons Stockpile. In this paper we describe a suite of models for conducting detailed simulations of chemical demilitarization incinerator operation. The models contain 3D furnace and canister geometries and all of the relevant physics and chemistry. The destruction of chemical agent is predicted using non-equilibrium chemistry models. Models have been developed for a Liquid Incinerator, Metal Parts Furnace, and a Deactivation Furnace System. Using computational chemistry methods, chemical kinetics have been developed that describe the incineration of organo-phosphorus nerve agent (GB, VX) and sulfur mustard (H, HD, HT). The models have been used to study a variety of scenarios to develop a deeper understanding of furnace operation and agent destruction when processing munitions or equipment containing or contaminated by chemical agent. Model results demonstrate the incinerators to be robust systems that destroy chemical agent in a safe and efficient manner.

1. INTRODUCTION

The U.S. stockpile of chemical weapons consists of munitions, including mines, rockets, artillery shells, and bombs containing warfare agents stored at eight sites in the continental United States. The chemical warfare agents (CWA) consist of mustard gas and other blister agents as well as organo-phosphorus nerve agents. Incineration was used to successfully destroy the stockpile at Johnston Island in the Pacific Ocean and is being used to destroy the stockpile at Tooele, Utah and Anniston, Alabama. Incinerators are under systemization at Umatilla, Oregon and Pine Bluff, Arkansas.

Through funding from a DoD SBIR award, Reaction Engineering International (REI) has developed advanced computer simulation tools for analyzing chemical demilitarization incinerators. The simulations are performed with a combination of detailed Computational Fluid Dynamic (CFD) models and fast running process (mass/energy balance) models (Bockelie, 2002; Denison et al., 2001, 2002, 2003, 2004). The CFD models include the detailed chemistry and physics required to analyze the incinerator units and corresponding afterburners within 3D furnace and canister geometries. The models include the full coupling of turbulent fluid mechanics, all modes of heat transfer (including radiation) and equilibrium combustion chemistry for agent and fuel. The models provide detailed information on the local gas properties, such as gas temperature, species concentrations (e.g., oxygen, agent, combustion products, and products of incomplete combustion), pressure, etc. The models also provide detailed information on the surface temperatures and heat fluxes to the furnace walls, munitions and equipment within the incinerator.

Agent destruction within the furnaces and afterburners is predicted using non-equilibrium (finite rate) chemistry models integrated with the CFD models of the furnaces. Full and reduced chemical kinetic mechanisms are used to obtain a detailed description of the chemical agent destruction, including intermediate and final combustion products (Montgomery et al., 2003a-b; Bockelie et al., 2004b). The chemical kinetic mechanisms for the agents were developed using computational chemistry methods. Process models are used to model the gross behavior of less complex equipment within the incineration plant, such as the Pollution Abatement System (PAS).

The tools and models are incorporated into a user friendly, computational workbench environment to facilitate application of the models to problems of interest. The simulation tools have been used to analyze the performance and emissions from military incinerator units under a broad range of operating conditions and configurations for different munitions and storage containers (Montgomery et al., 2003a; O'Shea et al., 2003; Bockelie et al., 2003, 2004a,b,c).

In the following we provide, in order, our approach for modeling the incinerator systems, a description of the chemical kinetic mechanisms compute agent destruction, examples of the capabilities of the models and an overview of how the models have been applied to address specific incineration questions.

2. MODELING APPROACH

The baseline incineration plants used within the U.S. are derived from the experiences and lessons learned from the Johnston Island facility. The baseline configuration consists of three incineration systems:
- The Liquid Incinerator Chamber (LIC) used to incinerate liquid CWA drained from munitions and bulk containers;

REACTION
ENGINEERING
INTERNATIONAL

Report Documentation Page		Form Approved OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **00 DEC 2004**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**	
4. TITLE AND SUBTITLE **Advanced Computer Simulations Of Military Incinerators**			5a. CONTRACT NUMBER
			5b. GRANT NUMBER
			5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)			5d. PROJECT NUMBER
			5e. TASK NUMBER
			5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Reaction Engineering International Salt Lake City, UT 84101; Carmagen Engineering, Inc Rockaway, NJ 07866; Cornell University Ithaca, NY 14853; New Jersey Institute of Technology Newark, NJ 07102**			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release, distribution unlimited**			
13. SUPPLEMENTARY NOTES **See also ADM001736, Proceedings for the Army Science Conference (24th) Held on 29 November - 2 December 2005 in Orlando, Florida. , The original document contains color images.**			
14. ABSTRACT			
15. SUBJECT TERMS			

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT **UU**	18. NUMBER OF PAGES **8**	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**			

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

- The Metals Parts Furnace (MPF) used to decontaminate drained shells, bulk containers, and self generated wastes; and
- The Deactivation Furnace System (DFS) used to deactivate energetic materials (propellants, fuses) used in the munitions.

In the following we describe our approach for modeling these systems.

2.1 MPF and DFS

The MPF and DFS require a time dependent simulation due to the periodic loading of munitions and sheared rocket pieces, respectively, combined with the burner and water spray control used to maintain the furnace operating temperature. To represent the time dependent nature of the MPF and DFS in an efficient manner, we utilize a combination of a transient "zonal" model and a steady state CFD model. The transient zonal model captures the time dependent effect on the overall furnace/afterburner temperature and gas composition due to sudden changes in agent release rate, burner turndown and water spray flows. The conditions predicted by the transient zonal model are subsequently used to define the boundary conditions for a steady state 3D CFD model that is used to compute the local mixing and destruction efficiency for a prescribed instant in time. The CFD model boundary conditions include the munitions metal temperatures, agent release rate, fuel flow rate and water spray flow rate. This approach has proven quite successful and allows a broad range of scenarios to be modeled using desktop PCs to perform the simulations.

2.2 LIC

The LIC operates in steady-state. The flow rate of natural gas to the burners in the primary and secondary chambers are adjusted to maintain a furnace set point temperature based on the desired flow rate of agent and combustion air and the flow rate of spent decontamination solution injected into the secondary chamber. A steady-state, zero-dimensional (0D) process model is used as a preprocessor to calculate the necessary fuel flow rates to each chamber for use in the CFD models. These flows are calculated using a chemical equilibrium approach with wall heat transfer. Inputs to the process model include the flow rates for agent, combustion air and decontamination solution and the set point temperatures for the primary and secondary chambers. The model computes the natural gas flow rate needed to achieve the set point temperature at equilibrium and the equilibrium combustion gas composition at that temperature. The LIC CFD models use these inputs and calculated flow rates.

2.3 Agent Destruction Modeling Approach

Finite rate kinetic calculations are performed to predict the agent destruction as a post process to the combustion and flow calculation. Three approaches are available:

1) integrate the complete detailed kinetic mechanism along a streamline in the furnace. This approach accounts for pyrolysis and oxidation, including the effects of local radical concentrations (e.g., O, H and OH) and temperature interpolated from the combustion flow field. Streamlines are initialized with pure agent. By performing the calculation with detailed chemistry, the intermediate and final products of agent destruction are predicted.

2) use a CFD based post-processor that includes a reduced chemical kinetic mechanism in the solution of the conservation equations for species. This approach computes the agent destruction within the entire flowfield. The reduced mechanism is created by assuming that many of the radical and intermediate species are in quasi-steady state (QSS). This assumption, which is valid under many combustion conditions, replaces a differential equation for a specie's concentration with an algebraic equation. The species to be approximated as being in QSS are selected using a genetic optimization algorithm that minimizes the difference between detailed and reduced chemistry for conditions of interest. A reduced mechanism approximates the accuracy of the original detailed mechanism, but requires tracking far fewer chemical species. The effects of local radical concentration are included in the calculations and intermediate and final products are also computed.

3) solve a single conservation equation for only the parent molecule of the agent by applying only the initial destruction paths in the detailed mechanism. The dominant step is the unimolecular decomposition. Radical attack is included, but because the radical concentrations are obtained from the equilibrium combustion solution the resulting radical concentrations are conservatively low. Using this approach allows performing a very fast-running CFD simulation to estimate destruction of the agent compound (i.e., from lethal to non-lethal) within the furnace, but does not provide information on intermediate or final products.

3. DETAILED CHEMICAL KINETIC MECHANISMS FOR CWAs

The combustion kinetics of CWAs are a key part of simulating the incineration process. Unfortunately, reliable experimental data for reaction rates of CWAs are not available. To our knowledge, no experiments using CWAs are being performed or are planned. Hence, as part of the SBIR project, computational chemistry methods were employed to develop the chemical kinetic mechanisms that describe CWA destruction. Development of the CWA kinetic mechanisms leveraged work originally performed under a US Army funded Multiple University Research Initiative (MURI) grant (ARO Grant DAAL03-92-G-0113), led by Prof. Fred Gouldin; the MURI project laid the groundwork for developing a basic understanding of the incineration chemistry involved in destroying CWA.

Modern computational chemistry methods have proven their ability to accurately calculate chemical reaction rates. These methods have been used to update a previously published detailed chemical kinetic mechanism for the pyrolysis and oxidation of GB (Glaude et al., 2002), and to develop new mechanisms for VX and mustard agents (Montgomery et al., 2003b). Combustion

kinetics of mustard agents have also been extended to include new kinetics and thermodynamic properties for impurities occurring in HD and H mustard and for the major components and impurities of HT.

The detailed chemical kinetic mechanisms that describe CWA destruction were developed from *ab initio* and density functional computational chemistry calculations and verified by comparison to high quality experimental data for similar substances where available. The types of calculations used to determine these rates are used in hundreds of journal publications yearly in the field of chemical kinetics. The new kinetics and thermodynamic properties for CWAs and their decomposition and oxidation products have been combined with kinetics from the literature for oxidation of hydrocarbons, phosphorus, sulfur, fluorine, chlorine, and nitrogen. The result is a complete set of rates of decomposition and oxidation of CWAs and their products beginning with the agents and ending with the stable oxides (Bockelie et al., 2004b).

The CWA chemical kinetic mechanisms have undergone critical review by an expert advisory panel, consisting of Prof. Fred Gouldin (Cornell University), Prof. Joe Bozzelli (NJIT), Dr. Wing Tsang (NIST), Dr. Charlie Westbrook (LLNL), Dr. Dick Magee (Carmagen) and Prof. Adel Sarofim (REI/U. of Utah).

3.1 GB

A detailed chemical kinetic mechanism for oxidation of nerve agent GB was developed by Glaude et al. (2002). The most important reaction for the destruction of GB was found to be a six-center unimolecular retro-ene reaction eliminating propene (see Figure 1). To improve the precision of the dominant rate expression for GB destruction, high level density functional calculations have been performed on the retro-ene and bond cleavage reactions of GB (Montgomery et al., 2003a). After enhancements for improved phosphorus chemistry, the detailed mechanism for GB destruction contains 129 species and 671 reactions.
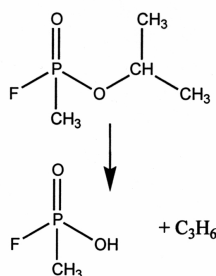

Fig. 1. Dominant destruction pathway for GB (Glaude et al., 2002)

3.2 VX

The dominant pathway for VX decomposition is a six-center molecular elimination reaction (see Figure 2). The recommended rate constant for this reaction is based on three high level density functional calculations. The calculated enthalpy differences between the VX molecule and the transition state from the three calculations were averaged and the calculated rate constants were matched

using curve fitting. The detailed mechanism includes 218 species and 1182 reactions.
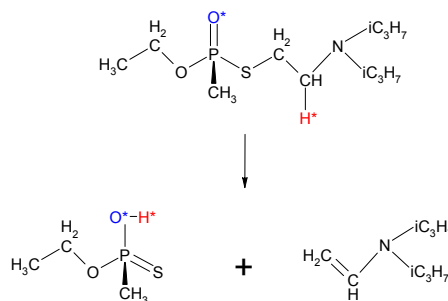

Fig. 2. Dominant destruction pathway for VX.

3.3 HD

HD mustard is modeled as a four species blend of compounds that includes the mustard molecule [bis(2-chloroethyl) sulfide] and three impurities. The impurities are by-products of the mustard manufacture as well as products of aging. The modeled impurities were selected based on a sampling campaign that characterized the content of munitions and bulk containers containing mustard agent [NRC, 2001; EG&G, 2003; ACWA, 2003a]. As with nerve agent, HD destruction is dominated by a unimolecular retro-ene reaction (in this case, eliminating HCl) for the mustard molecule as well as for each impurity. The detailed mechanism for describing the pyrolysis and oxidation of HD mustard includes 109 species and 477 reactions. A discussion of this kinetic mechanism is available in the open literature (Montgomery et al., 2003b).

3.4 H

H mustard is modeled as a five species blend of compounds that includes the mustard molecule [bis(2-chloroethyl) sulfide] and four additional impurities. The impurities are based on a sampling campaign that characterized the content of munitions and bulk containers containing mustard agent [NRC, 2001; ACWA, 2003b; Yang, 2004]. The kinetic mechanism is based on the mechanism developed for HD mustard and includes 143 species and 548 reactions.

3.5 HT

HT mustard is modeled as a five species blend of compounds that includes the mustard molecule [bis(2-chloroethyl) sulfide] and four impurities. The impurities are based on a sampling campaign that characterized the content of munitions and bulk containers containing mustard agent [ACWA, 2003a]. The kinetic mechanism is based on the mechanisms developed for HD and H and contains 165 species and 657 reactions.

3.6 Calculations Using the Detailed Models

The detailed kinetic models can be used to predict agent destruction, formation of products of incomplete combustion (PICs), and final product speciation as functions of combustion conditions (stoichiometry, temperature history, etc.). Figure 3 shows calculated

destruction of VX, GB and mustard agents in a plug flow reactor with a 2-second residence time as functions of temperature. These calculations can also be used to rank CWAs on the Incinerability scale of Taylor et al. (1990). Table 1 compares destruction temperatures for CWAs calculated with the detailed mechanisms with the temperatures and rankings of well-known compounds.
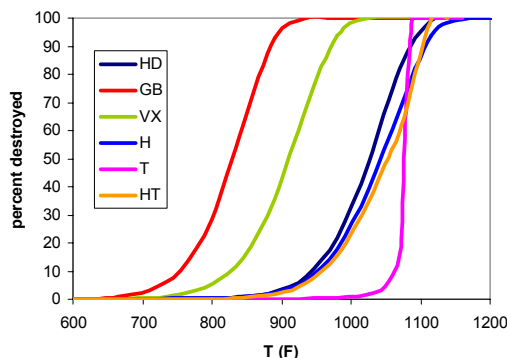

Fig. 3. Calculated destruction of agents VX, GB, H, HD, T, and HT in a plug flow reactor with a 2-second residence time as functions of temperature.

Table 1. Comparison of calculated T99(2) (temperatures for 99% destruction in 2 seconds) and associated incinerability rankings with published values for other compounds.

Compound	T99(2)	Class
Benzene	1150 C	1
Toluene	895 C	2
Vinyl Chloride	770 C	3
Trichloroethane	635 C	4
HD	628 C	4
H	603 C	4
HT	578 C	5
T	562 C	5
Chloroform	545 C	5
VX	541 C	5
Hexachloropropene	505 C	5
GB	491 C	5
Strychnine	320 C	6

4. INCINERATOR MODELS – EXAMPLE CALCULATIONS

In this section, we provide an example of the type of calculations that can be performed for the MPF, DFS and LIC models.

4.1 MPF Model

The metal parts furnace is used for decontamination of relatively inert munitions bodies, containers and self generated wastes. Firing an auxiliary fuel with air provides high temperature combustion products. Trays pass intermittently through the furnace, which typically has a set point gas temperature of 1600 °F. The furnace residence time is sufficient to drive off and destroy the agent and achieve 5X decontamination for all materials on the tray (i.e., materials maintain a temperature of at least 1000 °F for 15 minutes). A tray of munitions is introduced

from an airlock into the first zone where the agent in the munitions or containers is vaporized and combusted (for baseline operation). The tray then passes to the second zone where the temperature of the munitions or containers continues to rise, destroying any residual agent. The last zone is used to provide the required 5X decontamination. An airlock (not shown) following the third zone is used to ensure that residual agent vapors cannot escape the furnace. For baseline operation, every zone contains one tray of projectiles. The bursters are removed from the munitions prior to processing.

Figure 4 illustrates the agreement between measured data and values predicted by the nodal transient model when processing undrained (i.e., 100% full) 4.2in HD mortars in the JACADS MPF (note: the MPF at JACADS was fired with fuel oil). Overall there is good agreement of the agent vaporization rates (based on the shape of the O_2 profile) and on the water spray that is used to control the temperature in the MPF. The onset of vaporization calculated by the transient model occurs at about the same time delay as the measured data, or about 6 minutes after the trays are introduced into the furnace.
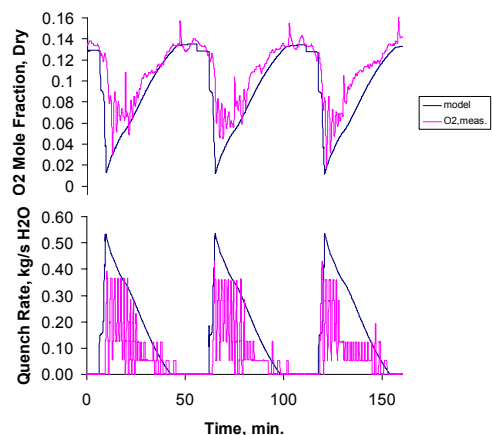

Fig. 4. Comparison of model calculations with test data of full 4.2in. HD mortars in JACADS MPF.

The CFD models of the furnace can be executed at any desired point in time using information extracted from the transient nodal model as boundary conditions. Figures 5 and 6 show the temperature and oxygen fields in the MPF primary furnace and afterburner at the peak total agent vaporization rate. Although not shown, the JACADS data exhibited a temperature spike (~2150 °F) in the cross-over duct at the time of peak vaporization rate. This spike is probably due to the combustion of unburned intermediate pyrolysis products coming from substoichiometric regions in the primary furnace. This is consistent with the low oxygen levels and temperatures entering the cross-over duct as shown in Figures 5 and 6. Figure 7 shows the agent concentration in the furnace at the same point in time. This calculation was performed using a reduced chemical kinetic mechanism. The agent concentration was also calculated using the parent molecule destruction and streamline methods. The result is essentially the same as that shown in Fig. 7. The figure

demonstrates that the agent is destroyed to below the detect limit (~1 ppb) prior to reaching the cross-over duct.

The MPF has proven to be a very robust furnace in which more efficient processing could be achieved to reduce the overall schedule for destroying the stockpile.
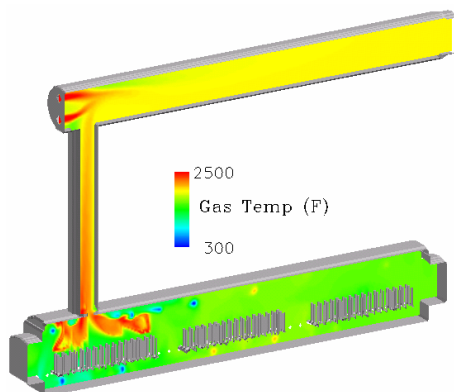

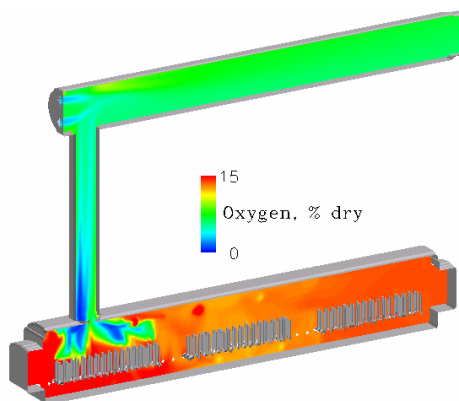Fig. 5. Predicted gas temperature distribution in the MPF for processing full 4.2in. HD mortars.

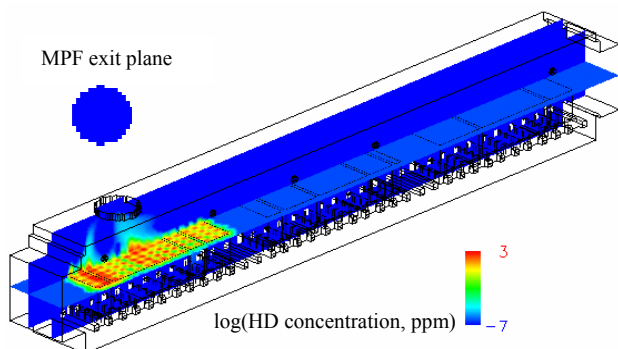Fig. 6. Predicted oxygen concentration in the MPF for processing undrained 4.2in. HD mortars.

Fig. 7. Predicted agent concentration in the MPF primary furnace for processing undrained 4.2in. HD mortars at the time of total peak vaporization rate.

4.2 DFS Model

The DFS incinerator is a gas-fired counterflow rotary kiln, or retort, designed to treat energetics (fuses, boosters, bursters, and solid rocket propellant). Energetics are contained in thin-walled metallic housings that are sheared into pieces prior to processing; otherwise confined energetics would detonate in the kiln rather than burn. Rocket pieces are dumped into the kiln at the feed end through two feed chutes. The number of rockets fed per hour can range between 1 and 40 depending on the retort operating conditions. Firing an auxiliary fuel with air provides high temperature combustion products at the discharge end. The burner fuel flow rate is controlled to maintain a set point temperature of about 1000 $^\circ$F. In addition to the burner air, negative pressure draws shroud air from the surroundings, which flows over the exterior of the kiln shell for cooling and then is used for combustion air. The rocket pieces are carried through the kiln via spiral flights or helical baffles as the kiln is rotated. Upon completion of energetics combustion, the rocket pieces fall from the kiln on to a heated discharge conveyor (HDC), which heats the rocket pieces to achieve the 5X criteria (i.e., 1000 $^\circ$F for 15 minutes).

As part of model benchmarking, model results and data from JACADS (three second resolution) for processing drained (i.e., 1 % residual agent) M55 GB rockets were compared. Figure 8 shows a comparison of the measured kiln exit oxygen from JACADS with the kiln exit oxygen calculated by the transient model over several cycles. The agreement is quite good. Model adjustments were made only to the exposed propellant area versus time profile, propellant linear burn rate, and shroud airflow to provide this agreement. Data were not available for the shroud airflow rate.
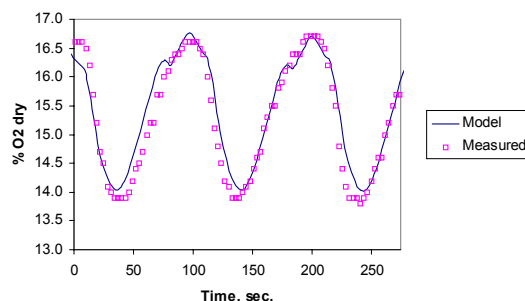

Fig. 8. Comparison of kiln exit gas oxygen between the transient model and measurements.

Agent destruction along streamlines in the kiln is shown in Figure 9 for processing rates of 33 rockets/hr and 1 rocket/hr. These streamlines were started at the location of the rocket pieces with the largest agent release rate at the time selected. An agent mass fraction of unity was used as the initial condition. The model predicts very rapid agent destruction due to the high local temperatures along three of the four streamlines shown. The high temperatures are caused by the large heat release from the energetics and burning of vaporized agent. Streamline 2 for the 33 rockets/hr case initially experiences a much lower temperature, and thus the agent survives for a longer period of time until the streamline temperature increases to a level sufficient for rapid destruction. Results for computing the agent destruction over the

http://wwww.reaction-eng.com

entire Eulerian flow field in the kiln using CFD based methods (i.e., using only the initial destruction kinetic steps of the detailed mechanism or a reduced chemical kinetic mechanism) are consistent with the streamline approach – the agent is destroyed rapidly. Furthermore, because the sources of agent are at nearly the same location as the sources from propellant combustion, the calculated maximum agent concentration is near the detect limit.
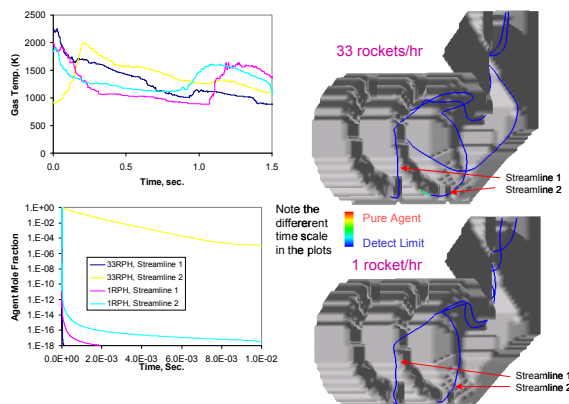

Fig. 9. Agent destruction calculated along streamlines in DFS kiln.

4.3 LIC Model

The liquid incinerator chamber (LIC) is used to dispose of chemical agent drained from bulk containers and munitions. The LIC consists of two natural-gas-fired combustion chambers. Air and natural gas are introduced into the primary chamber through a swirled burner, and liquid agent is injected at the burner through an air atomizer. Exhaust gas from the primary chamber passes through a duct to the secondary chamber where it encounters a high velocity natural gas burner. The purpose of this secondary chamber is to thermally treat any residual agent in the exhaust gas from the primary chamber. The burner in the secondary chamber is oriented offset from the chamber centerline, in a tangentially-fired manner, in order to promote a swirling flow field within the secondary chamber. In addition, spent decontamination solution can be injected through a port in the roof of the secondary chamber to incinerate the decontamination solution.

The gas temperature field in the LIC primary chamber, cross-over duct and secondary chamber are illustrated in Figure 10. Included in the figure are agent droplet trajectories in the near burner region in the primary chamber and droplet trajectories for spent decontamination solution injected from a port in the roof of the secondary chamber. As can be seen from Figure 10, the agent droplets vaporize very quickly, with the bulk of the combustion occurring within the burner cylinder; the combustion zone continues until the droplet trajectories terminate (i.e., droplets are vaporized). In the secondary chamber, a strong vortex-like flow field occurs due to the orientation of the burner and incoming flow from the cross-over duct (see discussion above). This swirled flow is apparent from the trajectories of the decontamination

solution droplets shown in the secondary chamber in Figure 10. Note that the decontamination solution spray acts to cool the combustion gases.
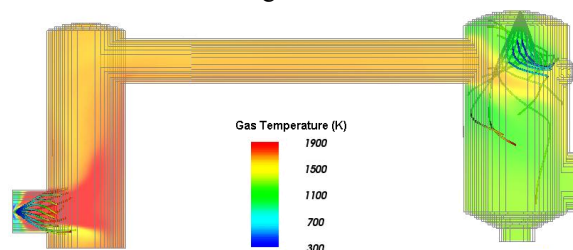

Fig. 10. Predicted gas temperature and spray droplet trajectories in LIC primary and secondary chambers for VX.

VX Agent destruction calculated using a CFD based method and parent molecule kinetic rates is shown in Fig. 11. This approach predicts that VX is destroyed below 1 ppb early in the burner cylinder. Beyond this region, the calculations indicate that trace amounts of agent (below 1ppb) continue to vaporize and breakdown. Similar results are obtained using reduced kinetic mechanisms; calculations of agent destruction along streamlines emanating from the burner predict the VX concentration is below detect limit within a few milliseconds. Likewise, simulations for other agents demonstrate that for baseline operating conditions the agent is destroyed to less than detect limit within the primary chamber.
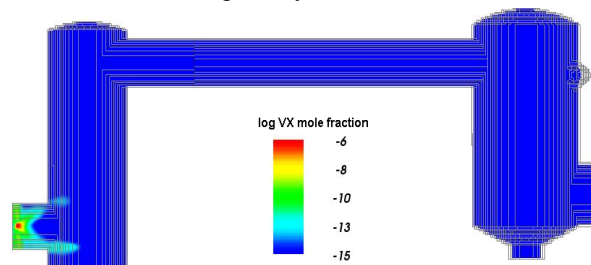

Fig. 11. VX destruction using parent molecule kinetic rates – LIC primary and secondary chambers.

5. IMPACT TO CHEM DEMIL PROGAM

The modeling capability developed within the SBIR project has been used in four "follow-on" projects conducted by REI that have benefited the Chem Demil program. The baseline incinerations plants cost approximately $300,000/day to operate. Hence, even small improvements that reduce the processing schedule can result in a significant cost reduction. The projects described below were performed with input and/or co-operation from: the Washington Demilitarization Company (WDC), site operator for three of the four incineration plants in the U.S.; Washington Group International (WGI), parent company of WDC and site operator for the Johnston Island facility (now decommissioned); and EG&G, Inc., site operator for the incineration plant at Tooele, Utah.

http://wwww.reaction-eng.com

REACTION ENGINEERING INTERNATIONAL

5.1 JACADS DAL Event

REI performed a special analysis of the operations at the JACADS incinerator (now decommissioned) after an agent release event in the JACADS MPF Discharge Air Lock (DAL). The agent release occurred when processing trays containing secondary wastes that were to be 5X decontaminated in the MPF. Due to the event, regulators imposed sanctions that resulted in severe restrictions on plant operation that would have added several months to the closure schedule for the plant. Utilizing the models described above, REI provided the technical backup used to convince regulators to modify the DAL clearance criterion which allowed JACADS to resume full operation (Montgomery et al., 2003a). The same DAL clearance criterion is being used at the other incineration sites. Altogether, this application of the modeling tools has provided significant cost savings to the Army (O'Shea et al., 2003).

5.2 UMCDF – Fate of Phosphorus

REI performed a special analysis for the fate of phosphorus through the UMCDF incinerators. In particular, differences in the metal removal efficiencies for phosphorus when processing organophosphorus agent (GB, VX) rather than organometallic phosphorus used in spiking compounds for surrogate trial burn tests were evaluated and explained (Bockelie et al., 2004c). Results of the analysis were used by UMCDF personnel as technical backup in negotiations with regulators that have resulted in UMCDF being able to take "credit" for emissions removal that occurs in the Particulate Filtration System (PFS), replace a planned surrogate trial burn with an agent trial burn and eliminate a planned high temperature test to evaluate metals removal. Hence, the provided analysis will shorten the schedule to bring the plant on-line.

5.3 RIM-65 Processing Undrained Mustard Projectiles with Solid Heels in the MPF

REI performed a special analysis to study the incineration of full trays of un-drained mustard munitions in the Metal Parts Furnace. Motivation for the project comes from the large number of 4.2in HD mortars and 155mm H projectiles located at the facilities in Tooele, Utah and Anniston, Alabama that can not be drained. Experience at Johnston Island demonstrated that undrained mustard munitions can be safely processed in the MPF. REI has made extensive use of the models developed in the SBIR project for the RIM-65 project. Analyses included "normal" processing (all agent vaporization in zone 1 of the MPF), optimized processing in which agent vaporization is overlapped between zone 1 and zone 2 of the MPF and several furnace upset scenarios. Model results have highlighted the robustness of the MPF and that processing full trays of undrained mustard munitions in a safe, efficient manner can be performed (Bockelie et al., 2004a). Although the project has not been completed, the model results clearly highlight the potential for improved processing that could shorten the schedule for plant operation.

5.4 SBIR Phase II Plus

REI was awarded an Army SBIR Phase II Plus to allow development of models to address problems of specific interest to CMA and the incineration site operators (WDC, EG&G). The problems were chosen to leverage REI's expertise in analysis and ability to solve industrial combustion problems. The Phase II Plus project consisted of four tasks (Bockelie et al., 2004b):

- Develop a detailed mechanism to describe the destruction of HT mustard (see section 3.5 above);
- Enhance the MPF sub-models to evaluate processing of partially drained HD ton containers that contain solid heels. Model results predict the required residence time to melt the solid heel, vaporize all agent and 5X decontaminate the metal ton container and inorganic residue that will remain in the container after vaporizing all agent. Optimized processing in which the process is overlapped between zone 1 and zone 2 was included in the analysis. The predictions show that for modest heel depths (six inches or less), processing the ton containers in the MPF is feasible.
- Investigate mercury capture (removal) in the PAS when processing HD. The analysis highlights the importance of the chlorine:mercury ratio on mercury capture. When processing liquid HD in the LIC, this ratio is sufficiently large that the mercury capture will be quite high in the LIC PAS. In contrast the chlorine:mercury ratio would be much lower when processing solid HD in the MPF and thus the mercury capture in the MPF PAS would be much lower. The degree of mercury removal by the brine in the PAS, or by carbon filters in a PFS located after the PAS, could impact the strategy and schedule for plant closure.
- Develop a CFD model of the Charcoal Micrconization System (CMS) Burner to investigate slagging problems during operation. The CMS burner is used to destroy charcoal from HVAC filters; thus it is potentially contaminated with agent and must be properly processed. At Johnston Island, slaging problems with the CMS burner resulted in significant down-time which adversely impacted the processing schedule. The REI analysis has identified the phosphorus in the ash of the coconut shell charcoal as the main cause of the slagging problems. Reacting, two phase flow CFD simulations of the burner processing the charcoal has resulted in recommendations to improve burner operation, such as tighter control of the micronizing mill to ensure elimination of large particles and alternative firing conditions to avoid conditions that aggravate the slagging. Improved performance of the CMS burner will help reduce the plant closure schedule.

5.5 EPA – Homeland Security R&D Center

The modeling tools described above are also being used in a program for the EPA Homeland Security Research and Development Center to assist in developing contingency plans for the thermal treatment in commercial incinerators of office building materials (e.g., rugs, wall paneling, wallboard) contaminated with chemical or biological agent due to a terrorist attack on an office building (Bockelie et al., 2005).

REACTION
ENGINEERING
INTERNATIONAL

CONCLUSION

This paper has described a suite of models, developed under US Army funding, to simulate the performance of the incinerator systems being used to destroy chemical weapons in the US Stockpile. The models include zonal models to obtain gross conditions and detailed CFD models of specific equipment components. Chemical kinetic mechanisms have been developed for nerve agents and sulfur mustard that describe the decomposition of the chemical agent during the combustion process, including intermediate and final combustion products. For normal operation, the models predict complete agent destruction in the incinerators.

The models have been used to develop a more detailed understanding of the key components and processes that occur within the incinerators as well as to address practical issues such as increasing furnace throughput, establishing agent monitoring conditions, and simulating incineration system upset conditions and failures that could lead to an agent release, so that appropriate design and operational modifications can be made to mitigate such occurrences. Altogether, the incinerator models demonstrate the beneficial use of applied science to assist the US Army meets a mission objective.

ACKNOWLEDGEMENT

REFERENCES

Assembled Chemical Weapons Alternatives (ACWA), Final Technical Report. Program Manager, 2003a: Summary of Engineering Design Study Projectile Washout System (PWS) Testing.

Assembled Chemical Weapons Alternatives (ACWA), Final Technical Report. Program Manager, 2003b: Summary of Engineering Design Study Munition Washout System (MWS) Testing.

Bockelie, M. J., 2002: Advanced Computer Simulations of Military Incinerators, *Twenty-third Army Sciences Conference*, Orlando, FL.

Bockelie, M. J., 2003: Modeling of the Metal Parts Furnace, *NRC Stockpile Committee Meeting*, Irvine, CA.

Bockelie, M.J. et al, 2004a (submitted May, 2004): RIM 65 - MPF Evaluation for Efficient Processing of Undrained Projectiles – Phase I Interim Report – TOCDF.

Bockelie, M.J. et al, 2004b (to be published December, 2004): Engineering Design Software for Military Incinerators, DAAD19-01-C0050, Final Report.

Bockelie, M.J. et al, 2004c (unpublished): Fate of Phosphorus When Processing Organophosphorus Agent (GB, VX) at UMCDF, whitepaper for WDC.

Bockelie, M.J. et al., 2005 (to be published March, 2005): Modeling Support for Incineration of Building, Final Report for EPA contract 4C-R010-NASX.

EG&G Defense Materials Inc., TOCDF, 2003: Project Report for Sampling and Analysis of Deseret Chemical Depot Mustard Ton Containers.

Denison, M. K., C. Montgomery, A. F. Sarofim, M. J. Bockelie, R. Magee, F. Gouldin, and G. McGill, 2001: Detailed Computational Modeling of Military Incinerators, *20th International Conference on Incineration and Thermal Treatment Technologies*, Philadelphia, PA.

Denison, M. K., C. J. Montgomery, A. F. Sarofim, M. J. Bockelie, A. G. Webster, and R. J. Mellon, 2002: Advanced Computational Modeling of Military Incinerators, *21st International Conference on Incineration and Thermal Treatment Technologies*, New Orleans, LA.

Denison, M. K., C. J. Montgomery, A. F. Sarofim, M. J. Bockelie, and A. G. Webster, 2003: Computational Modeling of a Chemical Demilitarization Deactivation Furnace System, *22nd International Conference on Incineration and Thermal Treatment Technologies*, Orlando, FL.

Denison, M. K., Sadler, B.A., Montgomery, C.J., Sarofim, A.F., Bockelie, M.J., 2004: Computational Modeling of a Liquid Incinerator Chamber, *23rd International Conference on Incineration and Thermal Treatment Technologies*, Orlando, FL.

Glaude, P. A., C. Melius, W. J. Pitz, and C. K. Westbrook, 2002: Detailed Chemical Kinetic Reaction Mechanism for Incineration of Organophosphorus and Fluoro-Organophosphorus Compounds, *Proceedings of the Combustion Institute*, **29,** 2469-2476.

Montgomery, C.J. et al, 2003a: Chemical Agent Decomposition Rates at Temperatures Anticipated in the Discharge Airlock, (unpublished), whitepaper for WGI.

Montgomery, C. J., M. J. Bockelie, A. F. Sarofim, J. Lee, and J. W. Bozzelli, 2003b: Thermochemical Properties, Reaction Paths and Kinetic Mechanism for Sulfur-Chloro Hydrocarbon Combustion: Part I: Thermochemistry and Pyrolysis of Chlorosulfides, *American Flame Research Committee International Symposium on Combustion*, Livermore, CA.

National Research Council, Board on Army Science and Technology, 2001: Analysis of Engineering Design Studies for Demilitarization of Assembled Chemical Weapons at Pueblo Chemical Depot.

O'Shea, L. et al, 2003: RIM 57 – Monitoring in the Metal Parts Furnace Discharge Airlock, WGI.

Taylor, P. H., Dellinger, B., and Lee, C. C., 1990: Development of a Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability, *Environ. Sci. Technl.*, **24**, 316-328.

Yang, Y.-C., 2004: Personal communication, NMR Analysis of MWS H Heel Samples.